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(54) Title: **NOVEL BRANCHED OXETANE POLYESTER**

(57) **Abstract:** A novel branched oxetane polyester having one or more oxetane groups is disclosed. Said branched oxetane polyester is the reaction product of at least one di, tri or polyhydric compound, at least one di, tri or polycarboxylic acid or an analogous alkyl ester, halide or anhydride, and at least one compound having at least one oxetane group and at least one hydroxyl group. Said di, tri or polyhydric compound works as an initiator, core or nucleus, from which at least two branches, built up from said di, tri or polycarboxylic acid or said analogous alkyl ester, halide or anhydride and said compound having said at least one oxetane group and said at least hydroxyl group, radiates.

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NOVEL BRANCHED OXETANE POLYESTER

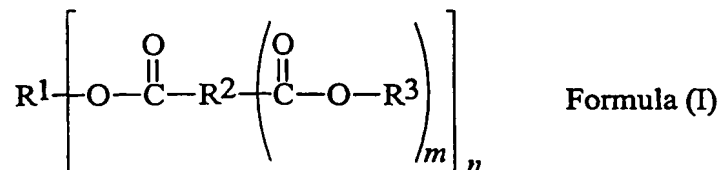
The present invention refers to a novel branched polyester having one or more oxetane groups (hereinafter called branched oxetane polyester). Said branched oxetane polyester is the reaction product of at least one di, tri or polyhydric compound, at least one di, tri or polycarboxylic acid or a corresponding alkyl ester, halide or anhydride, and at least one compound having at least one oxetane group and at least one hydroxyl group. Said di, tri or polyhydric compound works as an initiator, core or nucleus, from which at least two branches, built up from said di, tri or polycarboxylic acid or said ester, halide or anhydride thereof and said compound having said at least one oxetane group and said at least hydroxyl group, radiates.

Compounds having one or more oxetane groups, optionally in combination with one or more other reactive and/or functional groups, are per se known in the art and used in for instance coatings, inks, laminates, glues, dental materials and various binder and other resinous compositions. The present literature discloses a number of oxetane group(s) containing monomers, oligomers and polymers. Linear esters or polyesters having oxetane functionality are for instance disclosed by Bulacovschi et al in "*Substituted Oxetanes In Polymer Synthesis*"

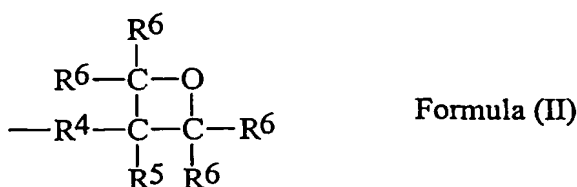
II¹, *Revue Roumaine de Chimie*, 1995, 40 (7-8), pp 737-741. said esters or polyesters are obtained from 3,3-bis(chloromethyl)oxetane and potassium terephthalate by nucleophilic substitution of chlorine in 3,3-bis(chloromethyl)oxetane. Branched oxetane polyesters wherein the branches radiates from an initiator, core or nucleus, derived from a di, tri or polyhydric compound, are not disclosed, discussed or contemplated. Triazine containing oxetanes are disclosed in US 3,449,340 as components in curing resin compositions. The compounds are obtained by addition of 2 to 3 moles of an oxetane functional alcohol, such as 3-hydroxymethyl-3-ethyloxetane, 3-hydroxymethyl-3-methyloxetane or 3-(α -hydroxyethyl)-3-methyloxetane, to 1 mole of triacryloylperhydrotriazine, and if only 2 moles of said oxetane functional alcohol are added, 1 mole of hydroxyl groups derived from a mono, di or trihydric aliphatic alcohol or ether alcohol, such as methanol, ethylene glycol and trimethylolpropane. EP 0 862 600 discloses thermosetting powder coating compositions comprising a cross linking agent having at least two oxetane groups. The cross linking agent is obtained by reacting an hydroxyfunctional oxetane, such as 3-ethyl-3-(hydroxymethyl)oxetane with an at least difunctional compound containing groups reactive towards hydroxyl groups, such as an aliphatic, cycloaliphatic or aromatic di, tri or tetraisocyanate. JP 11343346 and JP 11315181 disclose thermosetting oxetane compositions comprising (i) a polymer, having structural repeating units and an oxetane ring in a side chain of said repeating units, such as poly(3-ethyl-3-oxetanyl)methylmethacrylate, (ii) a carboxylic acid or anhydride such as phthalic anhydride and (iii) a compound having 2-3 thiol groups such as 2-dibutylamino-4,6-dimercapto-s-triazine and (iv) additionally a quaternary onium salt such as

a tetraphenylphosphonium halide. US 6,084,004 teaches curable compositions comprising a diaryliodonium compound, an α -dicarbonyl compound and a compound containing epoxide and/or oxetane groups. Disclosed oxetane groups containing compounds include compounds such as 1,10-decanediyl-bis(oxymethylene)-bis(3-ethyloxetane) and 1,4-butanediyl-bis(oxymethylene)-bis(3-ethyloxetane). Fluorinated oxetanes are disclosed in for instance WO 00/46270 teaching a polyester polymer including a polyoxetane block of repeating units derived from polymerising an oxetane monomer having at least one pendant $-\text{CH}_2\text{-O-(CH}_2\text{)}_n\text{-Rf}$ group wherein said Rf group is partially or fully fluorinated. Embodiments of the fluorinated oxetane polyester are obtained by reacting a polymer having repeating tetrahydrofuran units and repeating 2,2,2-trifluoroethoxymethyl-3-methyloxetane units with a diacid to form a half ester having acid end groups and subsequently reacting obtained product with additional diacids and diols to form polyester blocks. WO 00/34400 teaches radiation curable water based inks and coatings comprising an aqueous solution of a compound having at least two oxetane groups, such as 3-((oxiranylmethoxy)methyl)oxetane or 3-alkyl-((oxiranylmethoxy)methyl)oxetane wherein alkyl is $\text{C}_1\text{-C}_8$ and optionally a hydroxyalkyl oxetane, such as 3-ethyl-3-hydroxymethyloxetane. WO 00/02873 discloses an oxetane compound or copolymer having one oxetane group and one alkenyl group in combination with for instance an allyl, aryl, furfuryl, fluorine, fluoroalkyl or thienyl containing side chain. GB 729487 disclose a method for production of a polyester resin from an oxetane having at least two oxetane groups (oxycyclobutane rings), such as dioxaspiro heptane, and a carboxylic acid having at least two carboxyl groups. Branched oxetane polyesters wherein the branches radiates from an initiator, core or nucleus, derived from a di, tri or polyhydric compound, are not disclosed, discussed or contemplated. Curable cationic coating compositions containing oxetane compounds are for instance disclosed in GB 2310211 wherein a resin having oxetane as well as epoxy groups in the same molecule and an unsaturated monomer having an oxetane group at one end and an unsaturated group at the other end are used and in US 5,721,020 wherein compounds such as oxetanes having at least one oxetane group and at least one hydroxyl group or ether dimers or polymers thereof and/or compounds having at least one oxetane group and at least one $-\text{Si-O-}$ group are used.

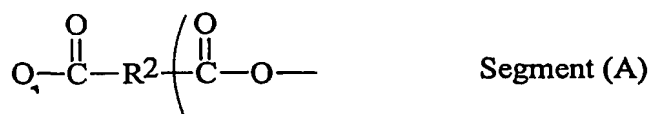
The present invention provides a branched polyester having one or more oxetane groups of a novel structure quite different from prior art oxetane functional monomers, oligomers and polymers. The structural difference between prior art and the branched oxetane polyester according to the present invention is from below disclosure and formulas obvious to those skilled in the art. The branched oxetane polyester is useful as a chemical intermediate, chemical crosslinker, curing agent and/or as a versatile component in for instance coatings, inks, glues and various resinous compositions comprising curable monomers, oligomers and/or polymers as well as in other applications known from said prior art. The novel branched oxetane polyester of the present invention is a compound of general formula



wherein m is an integer and at least 1, preferably at least 2, n is an integer and at least 2, R^1 is a group derived from a di, tri or polyhydric compound, R^2 is alkyl, aryl, alkylaryl or arylalkyl, R^3 is derived from a compound having at least one oxetane group and at least one hydroxyl group, whereby R^3 is a group of Formula (II)



wherein R^4 is alkyl, alkyloxyalkyl, alkylaryl, aryl, arylalkyl, aryloxyalkyl, R^5 is hydrogen, alkyl, alkoxy, aryl, aryloxy, and wherein each R^6 independently is hydrogen, alkyl, alkoxyalkyl, alkylaryl, aryl, arylalkyl or aryloxyalkyl, with the proviso that at least one of said alkyl, alkoxy or aryl has at least one carbon atom being hydroxyl substituted, and Segment (A)



of Formula (I) is derived from at least one di, tri or polycarboxylic acid or from at least one analogous anhydride, halide or alkylester.

Said di, tri or polyhydric compound works as an initiator, core or nucleus, from which at least two branches, built up from said di, tri or polycarboxylic acid or said analogous alkyl ester, halide or anhydride and said compound having said at least one oxetane group and said at least one hydroxyl group, radiates.

In above disclosure:

- alkyl is preferably C_1 - C_{24} , such as C_1 - C_{12} or C_1 - C_8 , linear or branched alkanyl or alkenyl,
- alkoxy is preferably ethoxy, propoxy, butoxy or phenylethoxy comprising 0.2-50, such as 0.2-20 or 0.2-10, alkoxy units or a combination of two or more of said alkoxy nominally comprising 0.2-10 units of respective alkoxy and nominally comprising a total of 0.2-20 alkoxy units, which means that for instance ethoxy units are combined with propoxy units or phenylethoxy units are combined with ethoxy units, such as ethoxylated propoxylates

and propoxylated phenylethoxylates, said alkoxy suitably being derived from one or more alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide and/or phenylethylene oxide, and

- oxyalkyl is preferably oxyethyl, oxypropyl, oxybutyl and/or a combination thereof.

Said di, tri or polyhydric compound, from which said substituent R¹ is derived, is in preferred embodiments of the present invention selected from the group consisting of

- i) a di, tri or polyhydric alcohol,
- ii) a dimer, trimer or polymer of a di, tri or polyhydric alcohol,
- iii) an adduct of a di, tri or polyhydric alcohol and at least one alkylene oxide,
- iv) an adduct of a dimer, trimer or polymer of a di, tri or polyhydric alcohol and at least one alkylene oxide,
- v) a di, tri or polyhydroxyfunctional ester or polyester of at least one carboxylic acid and a di, tri or polyhydric alcohol,
- vi) a di, tri or polyhydroxyfunctional ester or polyester of at least one carboxylic acid and a dimer, trimer or polymer of a di, tri or polyhydric alcohol,
- vii) a di, tri or polyhydroxyfunctional ester or polyester of at least one carboxylic acid and an adduct of di, tri or polyhydric alcohol and at least one alkylene oxide,
- viii) a di, tri or polyhydroxyfunctional ester or polyester of at least one carboxylic acid and an adduct of a dimer, trimer or polymer of a di, tri or polyhydric alcohol and at least one alkylene oxide,
- ix) a mono, di, tri or polyallyl ether of a tri or polyhydric alcohol, such as a monoallyl ether of glycerol, trimethylolethane or trimethylolpropane or a diallyl ether of di(trimethylolethane), di(trimethylolpropane) or pentaerythritol, and
- x) a mono, di, tri or poly(methallyl) ether of a tri or polyhydric alcohol, such as a mono(methallyl) of glycerol, trimethylolethane or trimethylolpropane or a di(methallyl) ether of di(trimethylolethane), di(trimethylolpropane) or pentaerythritol.

A di, tri or polyhydric alcohol as disclosed in sub-groups (i)-(x) above is in preferred embodiments for instance a 1,ω-diol, 5,5-di(hydroxyalkyl)-1,3-dioxane, 2-alkyl-1,3-propanediol, 2,2-dialkyl-1,3-propanediol, 2-hydroxy-1,3-propanediol, 2,2-dihydroxy-1,3-propanediol, 2-hydroxy-2-alkyl-1,3-propanediol, 2-hydroxyalkyl-2-alkyl-1,3-propanediol, 2,2-di(hydroxyalkyl)-1,3-propanediol. Alkyl is here C₁-C₂₄, such as C₁-C₁₂ or C₁-C₈, linear or branched alkanyl or alkenyl.

The most preferred di, tri or polyhydric alcohols can suitably be exemplified by mono, di, tri or polyethylene glycols, mono, di, tri and polypropylene glycols, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,6-cyclohexanedimethanol, 5,5-di(hydroxymethyl)-1,3-dioxane, 2-methyl-1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, 2-ethyl-

-2-butyl-1,3-propanediol, neopentyl glycol, dimethylpropane, glycerol, trimethylolethane, trimethylolpropane, diglycerol, di(trimethylolethane), di(trimethylolpropane), pentaerythritol, di(pentaerythritol), anhydroenneaheptitol, 2,2,6,6-tetramethylol cyclohexanol, sorbitol or mannitol.

An alkylene oxide as disclosed in sub-groups (iii), (iv), (vii) and (viii) above is preferably ethylene oxide, propylene oxide, butylene oxide and/or phenylethylene oxide, whereby said adduct comprises 0.2-50, such as 0.2-20 or 0.2-10, alkoxy units.

A carboxylic acid included in a hydroxyfunctional ester or polyester as disclosed in sub-groups (v)-(viii) above is preferably selected from the group consisting of adipic acid, azelaic acid, fumaric acid, maleic acid, phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, succinic acid, sebacic acid, diglycolic acid, trimellitic acid, citric acid and/or pyromellitic acid.

Said compound having at least one oxetane group and at least one hydroxyl group, from which substituent R³ is derived, is in various embodiments of the present invention preferably a 3-alkyl-3-(hydroxyalkyl)oxetane, a 3,3-di(hydroxyalkyl)oxetane or a 3-alkyl-3-(hydroxyalkoxy)oxetane or a dimer, trimer or polymer of a 3-alkyl-3-(hydroxyalkyl)oxetane, a 3,3-di(hydroxyalkyl)oxetane, a 3-alkyl-3-(hydroxyalkoxy)oxetane or a 3-alkyl-3-(hydroxyalkoxyalkyl)oxetane. Alkoxy and alkyl is here preferably as previously disclosed. Said oxetanes are suitably exemplified by 3-methyl-3-(hydroxymethyl)oxetane, 3-ethyl-3-(hydroxymethyl)oxetane and 3,3-di(hydroxymethyl)oxetane.

Segment (A) in Formula (I) above is in preferred embodiments advantageously derived from at least one di, tri or polyfunctional carboxylic acid, such as adipic acid, azelaic acid, fumaric acid, maleic acid, phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, succinic acid, sebacic acid, diglycolic acid, trimellitic acid, citric acid and/or pyromellitic acid, or from at least one analogous anhydride, halide or alkylester, such a dialkyl ester of adipic acid, azelaic acid, fumaric acid, maleic acid, phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, succinic acid, sebacic acid or diglycolic acid, a trialkyl ester of trimellitic acid or citric acid or a tetraalkyl ester of pyromellitic acid. Alkyl in dialkyl, trialkyl and tetraalkyl is preferably and independently linear or branched C₁-C₈ or C₁-C₄ alkanyl derived from at least one C₁-C₈ or C₁-C₄ linear or branched alkanol, such as methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol and/or *sec*-butanol.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilise the present invention to its fullest extent. The following preferred specific

embodiments are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever. In the following Examples 1-3 illustrate preparation of embodiments of the oxetane polyester of the present invention, said embodiments are prepared using embodiments of the process of the present invention.

EXAMPLE 1

95.6 g of pentaerythritol, 475.8 g of dimethyl terephthalate and 0.8 g of dibutyltin oxide were charged in a reaction vessel equipped with stirrer, heater, nitrogen inlet, cooler and receiver. The temperature was during 40 minutes raised to 190°C and kept at said temperature for alcoholysis. Formed methanol was continuously distilled off and removed. The alcoholysis was completed after 90 minutes and the temperature was reduced to 140°C. 243.6 g of 3-ethyl-3-(hydroxymethyl)oxetane was charged at said 140°C. The temperature was now during 100 min. raised to 220°C for alcoholysis. Formed methanol was continuously distilled off and removed. The alcoholysis was completed after 100 minutes and the temperature was reduced to 200°C. Vacuum (10 mm Hg) was now applied for 20 minutes to remove remaining formed methanol and possible unreacted reagents. Obtained product was subsequently cooled to room temperature. A hard, brittle resin was yielded. Said resin exhibited a viscosity of 400 mPas at 200°C and a molecular weight average (Mw) of 22315 determined by gel permeation chromatography using tetrahydrofuran as eluent.

EXAMPLE 2

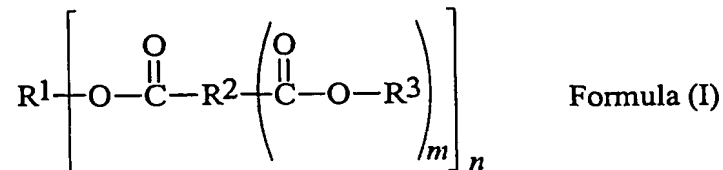
161.7 g of trimethylolpropane, 409.2 g of dimethyl succinate and 0.8 g of dibutyltin oxide were charged in a reaction vessel equipped with stirrer, heater, nitrogen inlet, cooler and receiver. The temperature was during 40 minutes raised to 190°C and kept at said temperature for alcoholysis. Formed methanol was continuously distilled off and removed. The alcoholysis was completed after 90 minutes and the temperature was reduced to 140°C. 243.6 g of 3-ethyl-3-(hydroxymethyl)oxetane was charged at said 140°C. The temperature was now during 100 min. raised to 220°C for alcoholysis. Formed methanol was continuously distilled off and removed. The alcoholysis was completed after 100 minutes and the temperature was reduced to 200°C. Vacuum (10 mm Hg) was now applied for 20 minutes to remove remaining formed methanol and possible unreacted reagents. Obtained product was subsequently cooled to room temperature. A high viscous resin was yielded. Said resin exhibited a viscosity of 120 mPas at 100°C and a molecular weight average (Mw) of 3204 determined by gel permeation chromatography using tetrahydrofuran as eluent.

EXAMPLE 3

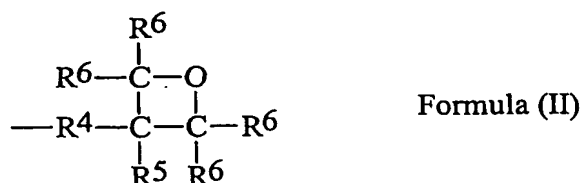
134.8 g of trimethylolpropane, 453.1 g of dimethyl terephthalate and 0.8 g of dibutyltin oxide were charged in a reaction vessel equipped with stirrer, heater, nitrogen inlet, cooler and receiver. The temperature was during 50 minutes raised to 210°C for alcoholysis and gradually further raised too a final temperature of 220°C. Formed methanol was continuously distilled off and removed. The alcoholysis was completed after 2.5 hours and the reaction mixture was cooled to room temperature. 193.3 g of 3-ethyl-3-(hydroxymethyl)oxetane was charged at room temperature. The temperature was now during 30 min. raised to 215°C for alcoholysis and gradually further raised to a final temperature of 220°C. Formed methanol was continuously distilled off and removed. The alcoholysis was completed after 4.5 hours and the temperature was reduced to 200°C. Vacuum (10 mm Hg) was now applied for 20 minutes to remove remaining formed methanol and possible unreacted reagents. Obtained product was subsequently cooled to room temperature. A solid resin was yielded. Said resin exhibited a viscosity of 240 mPas at 125°C.

CLAIMS

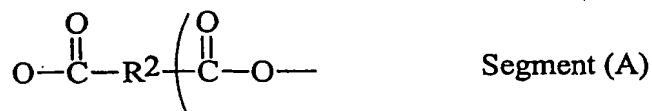
1. A branched oxetane polyester characterised in, that it has a general Formula of



wherein m is an integer and at least 1, preferably at least 2, n is an integer and at least 2, substituent R^1 is a group derived from a di, tri or polyhydric compound, substituent R^2 is alkyl, aryl, alkylaryl or arylalkyl, substituent R^3 is derived from a compound having at least one oxetane group and at least one hydroxyl group, R^3 being a group of Formula (II)



wherein R^4 is alkyl, alkyloxyalkyl, alkylaryl, aryl, arylalkyl, aryloxyalkyl, R^5 is hydrogen, alkyl, alkoxy, aryl, aryloxy, and wherein each R^6 independently is hydrogen, alkyl, alkoxyalkyl, alkylaryl, aryl, arylalkyl or aryloxyalkyl, with the proviso that at least one of said alkyl, alkoxy or aryl has at least one carbon atom being hydroxyl substituted, and wherein Segment (A)



of Formula (I) is derived from at least one di, tri or polycarboxylic acid or from at least one analogous anhydride, halide or alkylester.

2. A branched oxetane polyester according to Claim 1 characterised in, that said alkyl is C_1 - C_{24} , such as C_1 - C_{12} or C_1 - C_8 , linear or branched alkanyl or alkenyl, that said alkoxy is ethoxy, propoxy, butoxy, phenylethoxy comprising 0.2-50, such as 0.2-20 or 0.2-10, alkoxy units and that said oxyalkyl is oxyethyl, oxypropyl, oxybutyl and/or a combination thereof.

3. A branched oxetane polyester according to Claim 1 or 2 characterised in, that said di, tri or polyhydric compound, from which said substituent R^1 is derived, is selected from the group consisting of
- i) a di, tri or polyhydric alcohol,
 - ii) a dimer, trimer or polymer of a di, tri or polyhydric alcohol,
 - iii) an adduct of a di, tri or polyhydric alcohol and at least one alkylene oxide,
 - iv) an adduct of a dimer, trimer or polymer of a di, tri or polyhydric alcohol and at least one alkylene oxide,
 - v) a di, tri or polyhydroxyfunctional ester or polyester of at least one carboxylic acid and a di, tri or polyhydric alcohol,
 - vi) a di, tri or polyhydroxyfunctional ester or polyester of at least one carboxylic acid and a dimer, trimer or polymer of a di, tri or polyhydric alcohol,
 - vii) a di, tri or polyhydroxyfunctional ester or polyester of at least one carboxylic acid and an adduct of di, tri or polyhydric alcohol and at least one alkylene oxide,
 - viii) a di, tri or polyhydroxyfunctional ester or polyester of at least one carboxylic acid and an adduct of a dimer, trimer or polymer of a di, tri or polyhydric alcohol and at least one alkylene oxide,
 - ix) a mono, di or triallyl ether of a tri or polyhydric alcohol, and
 - x) a mono, di or tri(methallyl) ether of a tri or polyhydric alcohol.
4. A branched oxetane polyester according to Claim 3 characterised in, that said di, tri or polyhydric alcohol is a 1, ω -diol, 5,5-di(hydroxyalkyl)-1,3-dioxane, 2-alkyl-1,3-propanediol, 2,2-dialkyl-1,3-propanediol, 2-hydroxy-1,3-propanediol, 2,2-dihydroxy-1,3-propanediol, 2-hydroxy-2-alkyl-1,3-propanediol, 2-hydroxyalkyl-2-alkyl-1,3-propanediol, 2,2-di(hydroxyalkyl)-1,3-propanediol.
5. A branched oxetane polyester according to Claim 4 characterised in, that said alkyl is C_1 - C_{24} , such as C_1 - C_{12} or C_1 - C_8 , linear or branched alkanyl or alkenyl.
6. A branched oxetane polyester according to Claim 4 characterised in, that said at least one alkylene oxide is ethylene oxide, propylene oxide, butylene oxide and/or phenylethylene oxide, whereby said adduct comprises 0.2-50, such as 0.2-20 or 0.2-10, alkoxy units.
7. A branched oxetane polyester according to any of the Claims 3-6 characterised in, that said di, tri or polyhydric alcohol is a mono, di, tri or polyethylene glycol, a mono, di, tri or polypropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,6-cyclohexanedimethanol, 5,5-di(hydroxymethyl)-1,3-dioxane, 2-methyl-1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, dimethylpropane, glycerol, trimethylolpropane, trimethylolpropane,

diglycerol, di(trimethylolethane), di(trimethylolpropane), pentaerythritol, di(pentaerythritol), anhydroenneaheptitol, 2,2,6,6-tetramethylol cyclohexanol, sorbitol or mannitol.

8. A branched oxetane polyester according to any of the Claims 3-7 characterised in, that said at least one carboxylic acid is adipic acid, azelaic acid, fumaric acid, maleic acid, phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, succinic acid, sebacic acid, diglycolic acid, trimellitic acid, citric acid and/or pyromellitic acid.
9. A branched oxetane polyester according any of the Claims 1-8 characterised in, that said compound having at least one oxetane group and at least one hydroxyl group, from which substituent R^3 is derived, is a 3-alkyl-3-(hydroxyalkyl)oxetane, a 3,3-di(hydroxyalkyl)oxetane, 3-alkyl-3-(hydroxyalkoxy)oxetane or 3-alkyl-3-(hydroxyalkoxyalkyl)oxetane.
10. A branched oxetane polyester according any of the Claims 1-8 characterised in, that said compound having at least one oxetane group and at least one hydroxyl group, from which substituent R^3 is derived, is a dimer, trimer or polymer of a 3-alkyl-3-(hydroxyalkyl)oxetane, 3,3-di(hydroxyalkyl)oxetane, a 3-alkyl-3-(hydroxyalkoxy)oxetane or 3-alkyl-3-(hydroxyalkoxyalkyl)oxetane.
11. A branched oxetane polyester according to Claim 9 or 10 characterised in, that said alkyl is C_1 - C_{24} , such as C_1 - C_{12} or C_1 - C_8 , linear or branched alkanyl or alkenyl and that said alkoxy is ethoxy, propoxy, butoxy and/or phenylethoxy comprising 0.2-50, such as 0.2-20 or 0.2-10 alkoxy units.
12. A branched oxetane polyester according any of the Claims 1-8 characterised in, that said compound having at least one oxetane group and at least one hydroxyl group, from which substituent R^3 is derived, is 3-methyl-3-(hydroxymethyl)oxetane, 3-ethyl-3-(hydroxymethyl)oxetane or 3,3-di(hydroxymethyl)oxetane.
13. A branched oxetane polyester according to any of the Claims 1-12 characterised in, that Segment (A) of Formula (I) is derived from adipic acid, azelaic acid, fumaric acid, maleic acid, phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, succinic acid, sebacic acid, diglycolic acid, trimellitic acid, citric acid and/or pyromellitic acid.
14. A branched oxetane polyester according to any of the Claims 1-12 characterised in, that Segment (A) of Formula (I) is derived from a dialkyl ester of adipic acid, azelaic acid, fumaric acid, maleic acid, phthalic acid, isophthalic acid, terephthalic acid,

tetrahydrophthalic acid, hexahydrophthalic acid, succinic acid, sebacic acid or diglycolic acid, a trialkyl ester of trimellitic acid or citric acid or tetraalkyl ester of pyromellitic acid.

15. A branched oxetane polyester according to Claim 14 characterised in, that alkyl in said dialkyl, trialkyl or tetraalkyl independently is linear or branched C₁-C₈ alkanyl derived from at least one C₁-C₈ linear or branched alkanol.
16. A branched oxetane polyester according to Claim 15 characterised in, that said alkanol is methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol or *sec*-butanol.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 01/02224

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08G 65/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, PAJ, STN/CAPLUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 729487 A (HENKEL & CIE G.M.B.H.), 4 May 1955 (04.05.55) --	1-16
X	Revue Roumaine de Chimie, Volume 40, No 7-8, 1995, Victor Bulacovschi et al, "Polyesters Based on 3, 3-Bis(Chloromethyl) Oxacyclobutane and Potassium Terephthalate" page 737 - page 741 --	1-16
A	File WPI, Derwent accession no. 1999-544981, UBE IND LTD: "Thermosetting oxetane composition - useful for adhesives and paints", JP,A,11236438, 19990831, DW199946 --	1-16

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

12 March 2002

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 01/02224

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	File WPI, Derwent accession no. 1998-357551, UBE IND LTD: "Poly:esters containing hydroxymethyl groups in their side chains-are used for paints, coating agents, adhesives, films and fibres and have good hydrophilic and adhesive properties, dyeability, solubility in organic solvents and reactivity", JP,A,10139866, 19980526, DW199831 --	1-16
A	File WPI, Derwent accession no. 1999-367135, UBE IND LTD: "Thermosetting composition, for coatings, paint, etc. - comprises at least compound with specified oxetane rings in a molecule, compound with at least one oxiran ring in a molecule, etc.", JP,A,11140171, 19990525, DW199931 --	1-16
A	File WPI, Derwent accession no. 2000-058195, UBE IND LTD: "Heat curable oxetane compsn. used for coating mediums and electrical and electronic materials", JP,A,11315181, 19991116, DW200005 --	1-16
A	File WPI, Derwent accession no. 2000-102212, UBE IND LTD: "Heat curable oxetane composition comprising polymer having oxetane ring in side chain of repeating structural unit and compound having 2 or 3 thiol groups in molecule - cured product prepared by heating the heat curable oxetane composition", JP,A,11343346, 19991214, DW200009 --	1-16
A	WO 9719138 A1 (AKZO NOBEL N.V.), 29 May 1997 (29.05.97) --	1-16
A	WO 0046270 A1 (OMNOVA SOLUTIONS INC.), 10 August 2000 (10.08.00) -- -----	1-16

Form PCT/ISA/210 (continuation of second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT
Information on patent family members

28/01/02

International application No.

PCT/SE 01/02224

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
GB	729487	A	04/05/55	CH	140852 A	30/06/30
				CH	323614 A	15/08/57
				FR	1075180 A	13/10/54

WO	9719138	A1	29/05/97	DE	69605575 D,T	21/06/00
				EP	0862600 A,B	09/09/98
				ES	2141545 T	16/03/00
				US	6015864 A	18/01/00

WO	0046270	A1	10/08/00	EP	1064336 A	03/01/01
				EP	1161479 A	12/12/01
				US	2001051280 A	13/12/01
				WO	9945079 A	10/09/99
